ENERGY AND CHARGE TRANSPORT IN SELF-ASSEMBLING BIO-INSPIRED MATERIALS

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Recent research has focused on the self-assembly of organic molecules into supramolecular architectures in order to develop new materials for organic photonics and electronics. In organic photovoltaic materials, optimal performance requires both efficient charge generation and long distance charge transport. For example, the electronic properties of perylene-3,4;9,10-bis(dicarboximide) PDI chromophores can be tailored by changing substituents on the perylene chromophores, yielding both n-type and p-type materials. In particular, 1,7-bis(*N*-pyrrolidinyl)-perylene-3,4;9,10-bis(dicarboximide), 5PDI, displays an intense optical absorption band near 700 nm, which is significantly red shifted relative to the 550 nm absorbance of the corresponding 1,7-diphenoxy derivatives. We recently presented direct evidence using ultrafast transient absorption spectroscopy for symmetry breaking in the lowest excited singlet state of a symmetric cofacial 5PDI dimer (*cof*-$5PDI_2$), Figure 1, which results in the quantitative production of a $5PDI^{+\bullet}$-$5PDI^{-\bullet}$ radical ion pair in the low polarity solvent toluene with τ = 0.17 ps followed by charge recombination to ground state with τ = 220 ps. This is similar to the special pair of bacteriochlorophyll molecules that act as the primary electron donor in bacterial photosynthetic reaction center proteins, wherein the electronic excited state of the special pair is thought to have significant charge resonance character, which may result in symmetry breaking that leads to unidirectional electron transfer using one of the two sets of redundant electron acceptors within the protein.

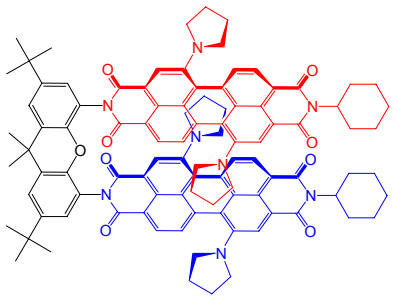

Figure 1. *cof*-$(5PDI)_2$

A critical step towards photofunctional devices is the ability to create increasingly larger arrays of interactive molecules. Covalent synthesis of large molecular arrays is highly inefficient and costly, thus making self-assembly the method of choice to achieve ordered architectures from functional building blocks. It is also very important to obtain structural information on these supramolecular assemblies. We have recently exploited small angle X-ray scattering (SAXS) at the APS at ANL to obtain this information. For example, we have synthesized a liquid crystal version of 5PDI by attaching 3,4,5-tris(dodecyloxy)phenyl groups to the imide nitrogen atoms (5PDI-LC), Figure 2, which absorbs light strongly from 550-750 nm. 5PDI-LC dissolves readily in methylcyclohexane (MCH) resulting in self-assembly into *H*-aggregates. SAXS data obtained on 10^{-4}M solutions of 5PDI-LC in MCH show that the aggregates are π-stacked monodisperse pentamers. Femtosecond transient absorption spectroscopy on solutions of $(5PDI\text{-}LC)_5$ in MCH shows evidence of charge separation occurring with τ = <150 fs between

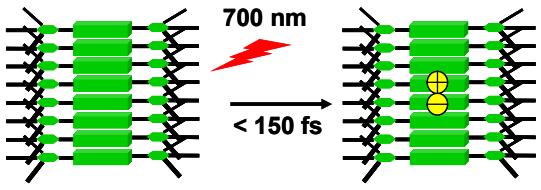

Figure 2. Stacked, cofacial 5PDI-LC molecules undergo ultrafast photoinduced charge separation.

adjacent stacked members of 5PDI-LC within the pentamer followed by charge recombination with τ = 860 ps. Differential scanning calorimetry and wide angle X-ray diffraction show that films of 5PDI-LC prepared from the melt exhibit a columnar discotic liquid crystalline mesophase from -50° to 364°. Transmission electron microscopy of 5PDI-LC films cast from solution show isolated bundles of columnar aggregates. $(5PDI\text{-}LC)_n$ is a potentially useful OPV material because efficient photoinduced charge generation is an intrinsic property of the assembly.

Self-assembly of robust perylenediimide chromophores is also used to produce an artificial light-harvesting antenna structure that in turn induces self-assembly of a functional special pair that undergoes ultrafast, quantitative charge separation. The structure consists of four PDI molecules attached to a single 5PDI core, which self-assembles to form $(5PDI\text{-}PDI_4)_2$ in toluene, Figure 3. The system is characterized using both structural methods (NMR, SAXS, mass spectroscopy, GPC) and photophysical methods (uv-vis, time-resolved fluorescence, and femtosecond transient absorption spectroscopy). Energy transfer from $(PDI)_2$ to $(5PDI)_2$ occurs with τ = 21 ps, followed by excited state symmetry breaking of $^{1*}(5PDI)_2$ to produce $5PDI^{+\cdot}$-$5PDI^{-\cdot}$ quantitatively with τ = 7 ps. The ion pair recombines with τ = 420 ps. Electron transfer occurs only in the dimeric system, and does not occur in the disassembled monomer, thus mimicking both antenna and special pair function in photosynthesis.

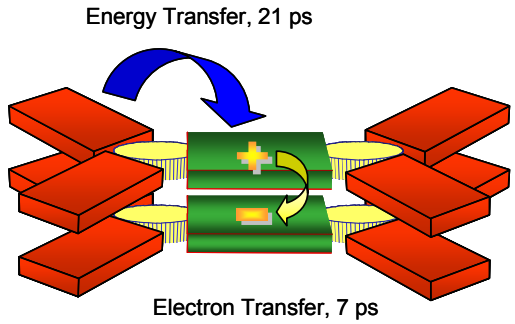

Figure 3. Self-assembled $(5PDI\text{-}PDI_4)_2$ light-harvesting and reaction center system.

Light harvesting in photosynthetic antenna proteins involves a series of highly efficient ultrafast energy transfers between spectroscopically different populations of chlorophylls. Several strategies have recently been employed to mimic this natural energy transfer process, including polymers**,** dendrimers, and oligomeric porphyrin arrays linked by covalent bonds or by self-assembly. In all of these systems, excitation energy transfer occurs from one molecule to another, while very few of them involve energy transfer from one very strongly-interacting chromophore aggregate to another such aggregate. Here we report the synthesis and characterization of a covalent zinc phthalocyanine-2,3,9,10,16,17,23,24-octcarboxytetraimide in which all four imide nitrogen atoms are substituted with PDI molecules to yield $(ZnPcIm_4\text{-}PDI_4)$. The individual molecules self-assemble into stacked heptamers, Figure 4, in solution as evidenced by SAXS and form long fibrous structures in the solid as evidenced by TEM. The $ZnPcIm_4$ and PDI molecules both stack in register with the same components in an adjacent covalent building block. Ultrafast energy transfer occurs with τ = 1.3 ps from the aggregated peripheral PDI chromophores to the core $ZnPcIm_4$ chromophore aggregate. Exciton hopping between the $ZnPcIm_4$ chromophores occurs with τ = 160 fs.

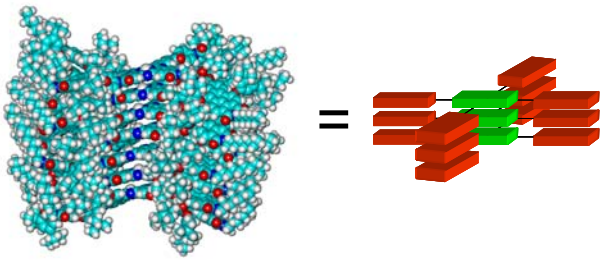

Figure 4. Stacked heptamer of $ZnPcIm_4\text{-}PDI_4$ molecules